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- 1 -

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Anticorrosion coating composition in aqueous dispersion comprising an organic titanate and/or zirconate

5 The present invention relates to an anticorrosion coating composition for metal parts, which is based on particulate metal in aqueous dispersion comprising an organic titanate or zirconate compatible in aqueous phase or in organic phase, optionally a silane-based binder, and water.

10 In the sense of the present invention, the expressions "titanate(s) compatible in organic phase" and "zirconate(s) compatible in organic phase" are understood as meaning every organic titanate and zirconate not compatible with water, that is to say not soluble in an aqueous composition  
15 and which in addition is sensitive to moisture and to water (hydrolysis reaction).

In the sense of the present invention, the expressions "titanate(s) compatible in aqueous phase" and "zirconate(s) compatible in aqueous phase" are understood as meaning  
20 every organic titanate and zirconate compatible with water, that is to say soluble or emulsifiable or dispersible in an aqueous composition. These are generally organic titanates and organic zirconates which have been stabilized by chelation. They are likewise named "chelated (organic)  
25 titanate(s)" and "chelated (organic) zirconate(s)".

The organic titanates, as well as the organic zirconates, compatible in organic phase can be used in anhydrous compositions as catalysts, reticulating agents, surface-treatment agents, adhesion promoters or anticorrosion  
30 agents. However, these organic titanates, as well as the organic zirconates, have the disadvantage of being very sensitive to water and to moisture inasmuch as they are hydrolysed very rapidly. For example, in the case of the

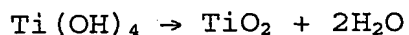
- 2 -

hydrolysis of tetra-n-butyl titanate, the following reactions occur:

1) conversion of the organic titanate to hydrated titanium oxide  $\text{Ti}(\text{OH})_4$ :



2) then, formation of titanium dioxide  $\text{TiO}_2$ :



10 In order to avoid the formation of titanium dioxide, the titanates and zirconates compatible in organic phase must thus be employed under rigorously anhydrous conditions. Consequently, the preparation of anhydrous compositions comprising a titanate or a zirconate compatible in organic phase is accompanied by very constraining handling  
15 precautions if it is wished to avoid the hydrolysis of the organic titanate to titanium dioxide on contact with air, moisture or traces of water.

The moisture resistance of titanates or zirconates compatible in organic phase can be improved by substituting  
20 two alkoxy groups by chelating agents. These chelating agents contain functional groups containing oxygen or nitrogen atoms which happen to stabilize the organic titanate or zirconate. These organic titanates or zirconates in chelated form can likewise be soluble in  
25 water, preferably in the presence of a weak acid of the acetic acid type. For example, the patent US 4 495 156 describes titanates in aqueous chelated form (TYZOR AA which is a titanate compatible in organic phase, TYZOR LA and TYZOR TE which are titanates compatible in aqueous  
30 phase) which allow the adhesion to a substrate of a composition comprising them to be improved.

The hydrolysis rate of the organic titanates and zirconates depends on the size and the complexity of the alkyl group

- 3 -

(the more the size of the alkyl group increases, the more the hydrolysis rate decreases). This is the reason why the organic titanates and zirconates in chelated form are less sensitive to hydrolysis than the tetraalkyl titanates or the tetra-alkyl zirconates.

The patent US 4 224 213 describes coating compositions comprising a short-chain alkyl silicate of formula  $\text{Si}(\text{OR})_4$ , a short-chain alkyl titanate or zirconate and zinc powder. This coating composition is reticulated by reaction of the silicate and the titanate with moisture from the air. The examples of this patent teach that the addition of silicate allows the moisture resistance of organic titanates to be improved. This coating composition is an organic composition which does not contain any water. The silicate, contrary to the silane, does not allow the adhesion of a composition comprising it to a substrate.

The patent EP 0 808 883 describes an aqueous coating composition based on particulate metal, free from chromium, intended to be applied to a substrate. This composition, once applied to the substrate, undergoes hardening in heat in order to provide the said substrate with protection against corrosion. In order to increase the corrosion resistance of this coated substrate, the coated substrate can optionally be coated with a supplementary layer comprising, for example, a silica material.

Surprisingly, the inventors have succeeded in incorporating into an aqueous composition organic titanates and/or organic zirconates, whether they are in chelated or non-chelated form and compatible or not compatible in aqueous phase. They have likewise discovered that the application to a metallic substrate of an aqueous coating composition

based on particulate metal comprising organic titanates and/or organic zirconates allows the resistance to corrosion of the substrate to be improved. The anticorrosion results being sufficient, a substrate coated  
5 by such a composition does not need any supplementary layer of anticorrosion coating. In addition, a coating is obtained whose flexibility and resistance to shocks is of very good quality, which is particularly advantageous in the case of anticorrosion coating of screws.

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The present invention relates to an anticorrosion coating composition of metal parts based on particulate metal in aqueous dispersion comprising, in the following proportions (percentages by mass):

- 15 - an organic titanate and/or zirconate : 0.3 to 24%;  
- a particulate metal or a mixture of particulate metals : 10 to 40%;  
- a silane-based binder : 1 to 25%;  
- water : q.s.p. 100%;

20 with the condition that the sum of the organic titanate and/or the organic zirconate and of the silane-based binder is between 5 and 25%.

The composition advantageously comprises 0.5 to 19% by weight, with respect to the total weight of the  
25 composition, of organic titanate and/or zirconate and 1 to 20% by weight, with respect to the total weight of the composition, of silane-based binder, on condition that the sum of organic titanate and/or zirconate and silane-based binder is between 7 and 20% by weight, with respect to the  
30 total weight of the composition.

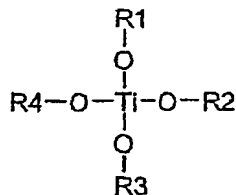
The organic titanates can be chosen from the group constituted by the organic titanates compatible in organic phase and the organic titanates compatible in aqueous

- 5 -

phase.

The titanates compatible in organic phase are advantageously  $C_1$ - $C_8$  tetraalkyl titanates which can be represented by the following formula (I'):

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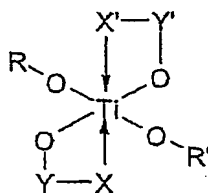


in which  $R1$ ,  $R2$ ,  $R3$  and  $R4$  independently represent an optionally substituted  $C_1$ - $C_8$  alkyl radical. The  $C_1$ - $C_8$  tetraalkyl titanate is advantageously chosen from the group comprising tetraethyl titanate (TET,  $Ti(OC_2H_5)_4$ ), tetra- $n$ -butyl titanate ( $T_nBT$ ,  $Ti(OC_4H_9)_4$ ) and octylene glycol titanate (OGT,  $Ti(O_2C_8H_{17})_4$ ).

The organic titanates compatible in organic phase can likewise be organic titanates in chelated form not compatible with water. As examples of organic titanates in chelated form not compatible with water (compatible in organic phase), it is especially possible to cite those marketed by Dupont de Nemours under the name TYZOR® AA (titanium acetylacetonate) or TYZOR® DC (diisopropoxy bisethylacetoacetato titanate).

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The titanates compatible in aqueous phase are advantageously chelated titanates, which can be represented by the following general formula (II'):



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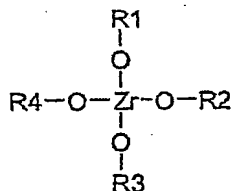
- 6 -

in which R and R' independently of one another represent an optionally substituted C<sub>1</sub>-C<sub>8</sub> alkyl radical, X and X' independently represent a functional group comprising an oxygen or nitrogen atom, and Y and Y' independently represent a hydrocarbon chain having 1 to 4 carbon atoms. X and X' advantageously represent an amino or lactate radical.

The organic titanate in chelated form compatible in aqueous phase is advantageously chosen from the group constituted by the triethanolamine titanates (TYZOR® TE and TEP marketed by Dupont de Nemours). As an example of organic titanates in chelated form compatible in aqueous phase, it is likewise possible to cite those marketed by Dupont de Nemours under the name TYZOR® TA (alkanolamine titanate in chelated form) and TYZOR® LA (chelate of titanate and lactic acid).

The organic zirconate can be chosen from the group constituted by the zirconates compatible in organic phase and the zirconates compatible in aqueous phase.

The organic zirconates compatible in organic phase are advantageously C<sub>1</sub>-C<sub>10</sub> tetraalkyl zirconates, which can be represented by the following formula (I):



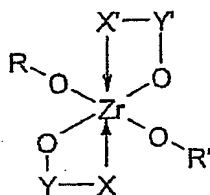
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in which R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> independently represent an optionally substituted C<sub>1</sub>-C<sub>10</sub> alkyl radical. The C<sub>1</sub>-C<sub>10</sub> tetraalkyl zirconate is advantageously chosen from the group constituted by tetra-n-propyl zirconate and tetra-n-

butyl zirconate.

The organic zirconates compatible in organic phase can likewise be organic zirconates in chelated form not compatible with water. As an example of an organic zirconate in chelated form not compatible with water (compatible in organic phase), it is especially possible to cite those marketed by Dupont de Nemours under the name TYZOR® ZEC (chelated diethyl citrate zirconate).

The organic zirconates compatible in aqueous phase are advantageously chelated zirconates which can be represented by the following general formula (II):



in which R and R' independently of one another represent an optionally substituted C<sub>1</sub>-C<sub>10</sub> alkyl radical, X and X' independently represent a functional group comprising an oxygen or nitrogen atom, and Y and Y' independently represent a hydrocarbon chain having 1 to 4 carbon atoms. X and X' advantageously represent an amino radical.

The chelated organic zirconate can advantageously be triethanolamine zirconate (TYZOR® TEAZ marketed by Dupont de Nemours). As an example of an organic zirconate in chelated form compatible in aqueous phase, it is likewise possible to cite that marketed by Dupont de Nemours under the name TYZOR® LAZ (chelate of zirconate and lactic acid).

The particulate metal of the coating composition can be chosen from the group constituted by the metallic pigments such as aluminium, manganese, nickel, titanium, stainless

- 8 -

steel, zinc, their alloys, as well as their mixtures. The particulate metal is advantageously chosen from zinc and aluminium, as well as their alloys and their mixtures or their alloys with manganese, magnesium, tin or Galfan. The  
5 particulate metal present in the composition is advantageously in powder form, different homogeneous or heterogeneous geometric structures, especially spherical, lamellar, lenticular forms or other specific forms. The particulate metal advantageously has a particle size of  
10 less than 100  $\mu\text{m}$ , even more advantageously less than 40  $\mu\text{m}$ . When the particulate metal is an alloy or a mixture of zinc and aluminium, the aluminium can optionally be present in very small quantities, for example 1 to 5% by weight of the particulate metal, while at the same time nevertheless  
15 providing a coating of shiny appearance. Customarily, the aluminium represents at least 10% by weight of the particulate metal, thus the weight ratio of the aluminium to the zinc is of the order of 1:9. On the other hand, for reasons of economy, the aluminium does not represent more  
20 than approximately 50% by weight of the total zinc and aluminium, so that the weight ratio of the aluminium to the zinc can reach 1:1. The content of particulate metal of the coating composition will not exceed approximately 40% by weight of the total weight of the composition in order to  
25 maintain the best coating appearance and will customarily represent at least 10% by weight in order to obtain a shiny coating appearance.

The metal can contain in minor quantity one or more solvents, for example dipropylene glycol and/or white  
30 spirit, especially when the metal has been prepared in lamellar form. The particulate metals containing solvents are customarily used in the form of pastes, which can be used directly with other ingredients of the composition.



However, the particulate metals can likewise be used in a dry form in the coating composition.

The said silane-based binder advantageously comprises a  
5 silane carrying at least one hydrolysable function in hydroxyl function chosen from a C<sub>1</sub>-C<sub>4</sub>, preferably C<sub>1</sub>-C<sub>2</sub>, alkoxy radical. The silane advantageously carries three hydrolysable functions in hydroxyl function, preferably identical. The silane can additionally carry an epoxy  
10 (oxirane) function, which favours the reticulation and adhesion to the substrate. "Hydrolysable function in hydroxyl function" is understood as meaning any chemical function capable of reacting with water in order to be converted into a hydroxyl function -OH.

15 The silanes, in the compositions of the present invention, serve as binding agents. They likewise allow the coating bath to be stabilized against a harmful autogenous reaction. The silane seems to bind and passivate the particulate metal, so that the stability of the bath of the  
20 coating composition is improved. In addition, it allows the adhesion of the coating and its resistance to corrosion to be improved. The silane advantageously represents 3 to 20% by weight of the total weight of the composition.

The silane is advantageously easily dispersed in the  
25 aqueous medium and is, preferably, soluble in such a medium. The silane used is advantageously a silane with an epoxy function chosen from di- or trimethoxysilane with an epoxy function and di- or triethoxysilane with an epoxy function, as well as their mixtures, in particular like  
30 beta-(3,4-epoxycyclohexyl)ethyl-trimethoxysilane, 4-(trimethoxysilyl)butane-1,2-epoxide or gamma-glycidoxypropyltrimethoxysilane.

If the organic titanate and/or zirconate used is an organic

titanate and/or zirconate compatible in aqueous phase, the silane is advantageously introduced in quantities such that the proportions by mass, in the final composition, of organic titanate and/or zirconate compatible in aqueous  
5 phase:silane are between 95:5 and 5:95.

The anticorrosion composition can be prepared by mixing an organic phase, especially comprising the silane and the particulate metal, with an aqueous phase, especially comprising water and the silane. The organic titanate  
10 and/or zirconate compatible in aqueous phase can be introduced either into the aqueous phase or into the organic phase.

When the organic titanate and/or zirconate compatible in aqueous phase is introduced into the organic phase, it is  
15 possible to substitute the silane, normally present in the organic phase, by this organic titanate and/or zirconate. The proportions by mass, expressed in dry parts, of organic titanate and/or zirconate and of silane are advantageously between 1:19 and 2:1, more advantageously between 1:16 and  
20 1:8.

When the organic titanate and/or zirconate compatible in aqueous phase is introduced into the aqueous phase, it is advantageously first co-hydrolysed with the silane, normally present in the aqueous phase. The mass proportions  
25 of organic titanate and/or zirconate and of silane during the co-hydrolysis are advantageously between 0.12 and 0.36, expressed in dry parts. The optimal conditions for the co-hydrolysis are obtained for a ratio by mass of 0.24 titanate and/or zirconate for 1 silane, the ratios being  
30 expressed in dry parts.

In order to co-hydrolyse the organic titanate and/or zirconate and the silane, the organic titanate and/or zirconate is introduced into the silane, in an appropriate

ratio, then they are co-hydrolysed by addition of 200 to 500% of water. It would appear that the duration of the co-hydrolysis reaction, that is to say the waiting time which follows the addition of the water, for example 30 or 90 min, does not have any influence on the properties of the co-hydrolysate obtained. If, instead of co-hydrolysing the silane and the organic titanate and/or zirconate compatible in aqueous phase, they are each hydrolysed separately, less satisfactory results are obtained in terms of product stability.

The addition of organic titanate and/or zirconate compatible in aqueous phase in the aqueous phase of the anticorrosion composition improves the anticorrosion properties of this composition more than if this titanate and/or zirconate had been added in the organic phase.

If the organic titanate and/or zirconate used is a titanate and/or zirconate compatible in organic phase, advantageously a  $C_1-C_8$  tetraalkyl titanate and/or zirconate, the silane is advantageously introduced in quantities such that the proportions by mass, in the final composition, of titanate and/or zirconate compatible in organic phase/silane are between 60/40 and 5/95, advantageously between 50/50 and 10/90.

The liquid medium of the coating composition is virtually always water or a combination of water and organic solvent. Other solvents can optionally be used but, preferably, only in very small quantities. Typically, the composition comprises 28 to 65% by weight of water, with respect to the total weight of the composition.

According to an advantageous embodiment of the invention, the coating composition additionally comprises 1 to 30% by weight of organic solvent or of a mixture of organic

- 12 -

solvents, with respect to the total weight of the composition. The organic solvents are advantageously chosen from the group constituted by the glycolic solvents such as the glycol ethers, in particular diethylene glycol, triethylene glycol and dipropylene glycol, the acetates, propylene glycol, polypropylene glycol, nitropropane, the alcohols, the ketones, propylene glycol methyl ether, 2,2,4-trimethyl-1,3-pentanediol isobutyrate (texanol), white spirit, as well as their mixtures.

10 Dipropylene glycol is particularly advantageous, especially for reasons of economy and of protection of the environment. The quantity of solvents is advantageously lower than 25% by weight, even more advantageously lower than 16% by weight, with respect to the total weight of the composition. When the metallic particles have been prepared in lamellar form in a solvent, the particulate metal resulting can be in the form of paste. It can then form a part of the organic solvent of the composition according to the invention.

20 According to an advantageous embodiment of the invention, the coating composition additionally comprises 0.1 to 7% by weight of molybdenum oxide, with respect to the total weight of the composition. The presence of molybdenum oxide  $\text{MoO}_3$  in the anticorrosion coating composition allows control of the sacrificial protection exerted by the particulate metal in suspension in the composition to be improved. The molybdenum oxide  $\text{MoO}_3$  is preferably used in an essentially pure orthorhombic crystalline form having a content of molybdenum of greater than approximately 60% by mass. Advantageously, the molybdenum oxide  $\text{MoO}_3$  will be used in the anticorrosion compositions in the form of particles of dimensions of between 5 and 200  $\mu\text{m}$ .

According to an advantageous embodiment of the invention, the coating composition additionally comprises 0.5 to 10% by weight of a reinforcing agent of the anticorrosion properties of the composition chosen from the group constituted by yttrium, zirconium, lanthanum, cerium, praseodymium, in the form of oxides or of salts. The said reinforcing agent of the anticorrosion properties of the composition is advantageously yttrium oxide  $Y_2O_3$  or cerium chloride. The said reinforcing agent of the anticorrosion properties of the composition can advantageously be combined with the abovementioned molybdenum oxide, in a mass ratio  $0.25 < \text{reinforcing agent of the anticorrosion properties: } MoO_3 < 20$ , advantageously  $0.5 < \text{reinforcing agent of the anticorrosion properties: } MoO_3 < 16$ , even more advantageously  $0.5 < \text{reinforcing agent of the anticorrosion properties: } MoO_3 < 14$ .

According to an advantageous embodiment, the coating composition additionally comprises a corrosion inhibitor pigment or corrosion inhibitor pigments such as the tri- or polyphosphate of aluminium, the phosphates, the molybdates, the silicates and borates of zinc, strontium, calcium, barium and their mixtures, at levels of the order of 0.2 to 4% by weight, with respect to the total weight of the coating composition.

The coating composition according to the invention can additionally comprise a thickening agent. The thickening agent is advantageously chosen from the group constituted by the cellulosic derivatives such as hydroxymethylcellulose, hydroxyethylcellulose, hydroxypropylcellulose, cellulose acetobutyrate, xanthan gum, the associative thickeners of polyurethane or acrylic type, the silicates such as the optionally treated silicates of magnesium and/or of lithium or the organophilic clays as

well as their mixtures. The content of thickening agent is advantageously lower than 7% by weight with respect to the total weight of the composition, advantageously between 0.005 and 7% by weight with respect to the total weight of the composition.

The coating composition according to the invention can likewise comprise a wetting agent, in a content advantageously lower than 4% by weight, more advantageously between 0.1 and 4% by weight, with respect to the total weight of the composition.

The composition according to the invention can also comprise a pH stabilizer such as boric acid, metaboric acid, tetraboric acid and boron oxide or boron salts. The composition can comprise, with respect to the total weight of the composition, 0.1 to 10% by weight, advantageously 0.2 to 5% by weight and even more advantageously 0.4 to 0.8% by weight, of pH stabilizer.

The composition can likewise comprise a pH modifier, generally chosen from the oxides and the hydroxides of alkali metals, advantageously lithium and sodium, the oxides and the hydroxides of metals belonging to groups IIA and IIB of the Periodic Table, such as the compounds of strontium, calcium, barium, magnesium and zinc. The pH modifier can likewise be a carbonate or a nitrate of the abovementioned metals.

The composition according to the invention can likewise comprise phosphates, substituents containing phosphorus, such as ferrophosphate (pigment), non-organic salts, in quantities lower than 2% by weight with respect to the weight of the composition.

The composition according to the invention is advantageously free from chromium VI. The composition can, however, contain chromium in soluble or non-soluble form

such as, for example, metallic chromium or chromium of oxidation state III.

The composition has good stability on storage, confirming the protective role of the silane towards a harmful  
5 reaction of the particulate metal with other ingredients of the composition. The silane likewise allows organic titanate to be stabilized.

The present invention likewise relates to the coating obtained by application of the coating composition  
10 according to the invention to a substrate, advantageously by spraying, soaking-draining or soaking-centrifugation, the coating layer then being subjected to a baking operation, preferably at a temperature of between 180°C and 350°C, for approximately 10 to 60 minutes, by supply of  
15 thermal energy, such as by convection or infrared, or for approximately 30 seconds to 5 minutes by induction.

According to an advantageous embodiment, the anticorrosion coating will result from an application operation involving, prior to a baking operation, a drying operation  
20 of the coated metallic parts, by supply of thermal energy, such as by convection, infra-red or induction, at a temperature of between 30 and 250°C, advantageously of the order of 70°C, in convection or in infrared for 10 to 30 minutes on line or for approximately 30 seconds to 5  
25 minutes by induction. Before coating, it is judicious in the majority of cases to eliminate the foreign matter from the surface of the substrate, especially by cleaning and careful degreasing. Under these conditions, the thickness of the dry coating film thus applied is between 3  $\mu\text{m}$  (11  
30  $\text{g}/\text{m}^2$ ) and 30  $\mu\text{m}$  (110  $\text{g}/\text{m}^2$ ) and preferably between 4  $\mu\text{m}$  (15  $\text{g}/\text{m}^2$ ) and 12  $\mu\text{m}$  (45  $\text{g}/\text{m}^2$ ), more particularly between 5  $\mu\text{m}$  (18  $\text{g}/\text{m}^2$ ) and 10  $\mu\text{m}$  (40  $\text{g}/\text{m}^2$ ).

The present invention also extends to the metallic

- 16 -

substrate, preferably of steel or steel coated with zinc or with a base layer of zinc deposited by different application methods including mechanical deposition, to cast iron and aluminium, provided with an anticorrosion  
5 coating according to the invention applied with the aid of the abovementioned compositions.

The metallic substrate can be previously treated, for example by a treatment with chromate or with phosphate. Thus, the substrate can be pretreated in order to have, for  
10 example, a phosphate coating of iron in a quantity of 0.1 to 1 g/m<sup>2</sup> or a phosphate coating of zinc in a quantity of 1.5 to 4 g/m<sup>2</sup>.

The present invention likewise relates to an aqueous  
15 composition of C<sub>1</sub>-C<sub>8</sub> tetraalkyl titanate and/or of C<sub>1</sub>-C<sub>8</sub> tetraalkyl zirconate, intended for the preparation of a coating composition for a metallic substrate in aqueous dispersion, prepared from a water-soluble organic solvent, a binder containing a silane carrying at least one  
20 hydrolysable function in hydroxyl function, a C<sub>1</sub>-C<sub>8</sub> tetraalkyl titanate and/or zirconate and water, in the following proportions (percentages by mass):

- water-soluble organic solvent : 0 to 20%
- silane-based binder : 20 to 50%
- 25 - C<sub>1</sub>-C<sub>8</sub> tetraalkyl titanate and/or zirconate : 5 to 25%
- water : 40 to 70%

In the context of the present invention, that is to say when the silane is found in the presence of C<sub>1</sub>-C<sub>8</sub> tetraalkyl titanate and/or zirconate, it would appear that  
30 the silane, in hydrolysed form before condensation, is capable of reacting with the abovementioned hydrated titanium oxide and/or zirconate in order to give a partially stable polymeric chain containing silicon and

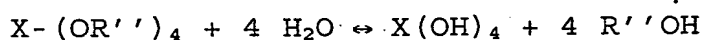


titanium and/or zirconate atoms. The silane then appears capable of stabilizing the C<sub>1</sub>-C<sub>8</sub> tetraalkyl titanate and/or zirconate. The chemical reactions could be written as follows:

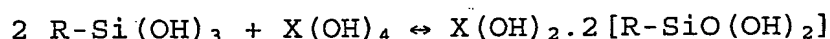
5 (1) Hydrolysis of the silane:



(2) Conversion of the organic titanate or zirconate to hydrated titanium or zirconium oxide:

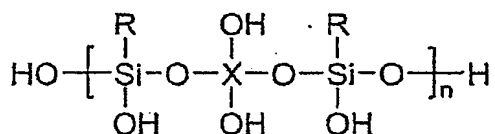


10 (3) Reaction between the hydrated titanium or zirconium oxide and the hydrolysed silane:



The silane and the organic titanate or zirconate thus associate in order to form the following partial polymeric chain: X(OH)<sub>2</sub>·2[R-SiO(OH)<sub>2</sub>]

The reaction can continue and lead to the formation of a polymeric chain of the following formula (III):



20

formula (III)

in which X represents Ti or Zr.

The water-soluble organic solvent is advantageously chosen from the group constituted by the glycolic solvents such as the glycol ethers, in particular diethylene glycol, triethylene glycol and dipropylene glycol, the acetates, propylene glycol, the alcohols, the ketones, propylene glycol ether, as well as their mixtures.

The silane carrying at least one hydrolysable function in hydroxyl function contained in the binder is advantageously

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chosen from a C<sub>1</sub>-C<sub>4</sub>, even more advantageously C<sub>1</sub>-C<sub>2</sub>, alkoxy radical. In addition, this silane advantageously carries an epoxy function. The said silane is preferably chosen from di- or trimethoxysilane with an epoxy function and di- or triethoxysilane with an epoxy function, as well as their mixtures, in particular gamma-glycidoxypropyl-trimethoxysilane or beta-(3,4-epoxycyclohexyl)ethyl-trimethoxysilane.

The C<sub>1</sub>-C<sub>8</sub> tetraalkyl titanate is advantageously chosen from the group comprising tetra-ethyl titanate (TET), tetra-n-butyl titanate (T<sub>n</sub>BT) and octyleneglycol titanate (OGT) and the C<sub>1</sub>-C<sub>8</sub> tetraalkyl zirconate is chosen from the group comprising tetra-n-propyl zirconate and tetra-n-butyl zirconate. In the aqueous composition, the ratio by mass of C<sub>1</sub>-C<sub>8</sub> tetraalkyl titanate and/or zirconate with respect to the silane is from 60/40 maximum, advantageously to 50/50 maximum, advantageously to 40/60 maximum.

The aqueous composition of C<sub>1</sub>-C<sub>8</sub> tetraalkyl titanate and/or C<sub>1</sub>-C<sub>8</sub> tetraalkyl zirconate can be prepared by mixing the silane-based binder, the said titanate or zirconate and, if necessary, the said water-soluble organic solvent, with a small quantity of water and then, by continuous progressive addition, at a low rate, of the remaining quantity of water.

In this stabilized form, the C<sub>1</sub>-C<sub>8</sub> tetraalkyl titanate and/or zirconate can, for example, then be introduced into a coating composition for a metallic substrate in aqueous phase, especially an anticorrosion coating composition based on particulate metal in aqueous dispersion, while limiting the formation of titanium dioxide.

The present invention finally relates to the use of the aqueous composition of C<sub>1</sub>-C<sub>8</sub> tetraalkyl titanate and/or C<sub>1</sub>-

- 19 -

C<sub>8</sub> tetraalkyl zirconate defined above in pretreatment for coatings or adhesives (polyurethane, acrylic, rubber...). This composition can also be used in posttreatment as a sealer based on metallic particles. This composition can  
5 likewise be used in passivation treatment for substrates based on steel, zinc, aluminium or steel covered with a zinc-based coating. This composition can finally be used in an additive in order to improve the adhesion of the coatings or adhesives (polyurethane, acrylic, rubber, ...) in aqueous phase.  
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The examples below show ways in which the present invention can be employed, but do not limit the present invention in any fashion.

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Preparation of the test panels:

Unless indicated otherwise, the test panels are typically stainless steel panels with a low carbon content, laminated in the cold. They can be prepared first of all by immersion  
20 in a cleaning solution. Then, the panels can be wiped with a cleaning pad and then rinsed with water and again immersed in the cleaning solution. After removal of the solution, the panels are rinsed with tap water and dried.

25 Application of the coating to the test panels and weight of the coating:

The clean parts are coated, in a typical fashion, by dipping then into the coating composition, by withdrawing and draining the composition in excess of this, several  
30 times with a moderate stirring action, and then by immediate baking or drying at ambient temperature or pre-hardening at a moderate temperature until the coating is dry to the touch and thus baked. The coating weights

- 20 -

(mg/cm<sup>2</sup>) are determined by comparative weighing before and after coating.

Test of resistance to corrosion (ISO 9227) and estimation:

The resistance to corrosion of coated parts is measured by means of the standard salt projection test (saline mist) for paints and varnishes ISO 9227. In this test, the parts are placed in a chamber maintained at a constant temperature where they are exposed to a fine projection (mist) of a 5% saline solution during specific periods of time, rinsed with water and dried. The extent of corrosion of the parts tested can be expressed in the form of the percentage of red rust.

Example 1: composition based on organic titanate compatible in organic phase

Constituent	Quantity (g/kg)
DPG (dipropylene glycol)	170.60
R40 <sup>5</sup>	13.00
R95 <sup>6</sup>	14.00
Dry aluminium <sup>2</sup>	25.00
Zinc paste <sup>1</sup>	245.00
Silane A-187 <sup>3</sup>	90.00
Dehydran <sup>10</sup>	5.00
Sodium silicate <sup>4</sup>	8.00
Boric acid	7.50
Molybdenum oxide <sup>9</sup>	8.00
T <sub>n</sub> BT (tetra-n-butyl titanate) <sup>8</sup>	40.00
Kelzan <sup>7</sup>	0.65
Water	373.30

Table 1

<sup>1</sup> Zinc in the form of paste to approximately 92% in white spirit

<sup>2</sup> Alu Chromal VIII powder marketed by Eckart Werke

<sup>3</sup> γ-glycidoxypropyltrimethoxysilane (Crompton)

<sup>4</sup> sodium silicate (Rhodia)

- 21 -

<sup>5,6</sup> Ethoxylated nonylphenol of R40 or of R95, supplier Oxiteno SA (Brazil)

<sup>7</sup> Kelzan/Rhodopol 23 from Rhodia

<sup>8</sup> supplier DuPont de Nemours

5 <sup>9</sup> supplier Lavollée

<sup>10</sup> supplier Cognis SA

**Example 2: composition based on organic titanate compatible in organic phase**

10 **a) composition:**

Constituent	Quantity (g/kg)
DPG (dipropylene glycol)	175.60
R40	13.00
R95	14.00
Dry aluminium	10.00
Zinc paste	260.00
Silane A-187	115.00
Silicate H300	10.00
Boric acid	9.50
Molybdenum oxide	10.00
T <sub>n</sub> BT (tetra-n-butyl titanate)	60.00
Kelzan	0.65
Water	317.25

Table 2

**b) Results of tests of resistance to saline mist**

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Duration of bath (days)	Density coating layer (g/m <sup>2</sup> )	Resistance to saline mist (hours)
5	23.6	2064
10	19.8	1944
15	20.1	1752

Table 3

Example 3: composition based on organic titanate compatible in organic phase

a) composition:

<i>Constituent</i>	<i>Quantity (g/kg)</i>
DPG (dipropylene glycol)	153.50
R40	13.00
R95	14.00
Dry aluminium	10.00
Zinc paste	260.00
Silane A-187	95.00
Silicate H300	10.00
Boric acid	9.50
Molybdenum oxide	10.00
TET (tetraethylene titanate) <sup>11</sup>	40.00
Kelzan	0.65
Water	379.35

Table 4

<sup>11</sup> supplied by DuPont de Nemours

b) Results of tests of resistance to saline mist

<i>Duration of bath (days)</i>	<i>Density coating layer (g/m<sup>2</sup>)</i>	<i>Resistance to saline mist (hours)</i>
5	20.8	456
10	19.7	360

Table 5

Example 4: process for preparation of an aqueous composition of tetrabutyl titanate, organic titanate compatible in organic phase:

The following reagents are mixed in order:

- a) 30.00 g of DPG (dipropylene glycol)
- b) 50.00 g of silane A-187

c) 20.00 g of TBT (tetrabutyl titanate)

The solution obtained is allowed to stand for 24 hours. The silane, introduced into the DPG before the T<sub>n</sub>BT, reacts with the water optionally present in the DPG. An uncontrolled reaction of the organic titanate with the water optionally present in the DPG is thus avoided.

100.00 g of water (=100.00 ml) are added respecting the following procedure:

- 10 i) add 0.125 ml of water dropwise and then allow the solution to stand for 10 minutes;
- ii) repeat step i) 5 times;
- iii) add the remaining quantity of water at a rate of 0.25 ml of water/minute/3 pulses, or approximately 15 0.083 ml of water every 20 seconds.

An aqueous composition of colourless organic titanate is obtained. Small crystals can appear; it is assumed that these are silica crystals.

The total duration of the preparation of the aqueous composition of organic titanate is approximately 20 7 h 30 min.

The aqueous composition of organic titanate is allowed to stand for at least 24 hours before optionally being introduced into a composition of anticorrosion coating.

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Example 5: process for preparation of an aqueous composition of organic titanate compatible in organic phase:

The process proceeds in the same fashion as in example 4 except that the quantity of T<sub>n</sub>BT introduced is 30.00 g. 30 An aqueous composition of colourless or sometimes slightly yellow organic titanate is obtained.

Example 6: process for preparation of an aqueous composition of organic titanate compatible in organic phase:

The process proceeds in the same fashion as in example 4 except that the quantity of T<sub>n</sub>BT introduced is 40.00 g. An aqueous composition of colourless or sometimes slightly yellow organic titanate is obtained.

Example 7: process for preparation of an aqueous composition of organic titanate compatible in organic phase:

The process proceeds in the same fashion as in example 4 except that the quantity of T<sub>n</sub>BT introduced is 40.00 g and the quantity of silane A 187 introduced is 70.00 g. An aqueous composition of colourless or sometimes slightly yellow organic titanate is obtained.

Example 8: corrosion resistance of a coating composition according to the invention based on organic titanate compatible in organic phase

The aqueous composition of organic titanate obtained in example 6 is introduced into an anticorrosion coating composition. Table 6 below indicates the formulation of the composition thus obtained and that of an anticorrosion coating composition of the prior art which do not contains organic titanate.



- 25 -

	Composition according to the invention A (g/kg)	Composition of the prior art B (g/kg)
DPG	160.60	160.60
Silane A 187	90.00	90.00
Water	383.30	421.10
Tetra-n-butyl titanate	40.00	-
Dry aluminium lamellae	25.00	25.00
Zinc paste	245.00	245.00
Molybdenum oxide	8.00	10.00
R40	13.00	13.00
R95	14.00	14.00
Dehydran	5.00	5.00
Sodium silicate	8.00	8.00
Boric acid	7.50	7.50
Kelzan	0.60	0.80

Table 6

The characteristics of composition A are reported in table 7 below:

5

Duration of the bath	adhesion	appearance	pH	density	% of solid	viscosity
72 hours	excellent	very good	7.7	1.35	36.1	54s (23°C)
5 days	excellent	very good	7.9	1.36	37.0	64s (23°C)
10 days	excellent	very good	8.1	1.39	38.3	70s (26°C)
15 days	excellent	very good	7.9	1.40	40.0	83s (26°C)
20 days	excellent	very good	7.8	1.42	41.9	121s (25°C)
25 days	excellent	very good	8.1	1.39	39.4	90s (24°C)

Table 7

- 26 -

The resistance of the two compositions to the saline mist is compared. The resistance values to the saline mist measured are summarized in table 8 below.

Composition according to the invention A		Composition of the prior art B	
Density coating layer (g/m <sup>2</sup> )	Resistance to saline mist (hours)	Density coating layer (g/m <sup>2</sup> )	Resistance to saline mist (hours)
16	704	16	208
20	880	20	260
24	1056	24	312
28	1232	28	364
32	1408	32	416
36	1584	36	468

5

Table 8

Satisfactory results for resistance to the saline mist are thus observed for the coating composition according to the invention. In fact, for a layer density of 24 g/m<sup>2</sup>, it is possible to attain a duration of resistance to the saline mist of greater than 1000 hours whereas for a composition without organic titanate the duration of resistance to the saline mist is only 312 hours. The addition of organic titanate allows the corrosion resistance of the coating to be at least tripled under these conditions.

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**Example 9: composition based on organic titanate compatible in organic phase**

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The addition of small quantities of organic titanate (10, 20 or 30 g/kg) allows the quantity of silane and of

- 27 -

molybdenum oxide to be introduced to be decreased, which allows a limitation of the costs, while conserving good anticorrosion results.

In the following examples of compositions (table 9), the quantity of silane is reduced to 44% by weight and the quantity of molybdenum oxide is reduced to 20% by weight, with respect to the quantities conventionally introduced into anticorrosion coating compositions.

	Composition C (g/kg)	Composition D (g/kg)	Composition E (g/kg)
DPG	160.60	160.60	160.60
Silane A 187	50.00	50.00	50.00
Water	453.20	443.20	433.20
Tetra-n-butyl titanate	10.00	20.00	30.00
Dry aluminium lamellae	25.00	25.00	25.00
Zinc paste	245.00	245.00	245.00
Molybdenum oxide	8.00	8.00	8.00
R40	13.00	13.00	13.00
R95	14.00	14.00	14.00
Dehydran	5.00	5.00	5.00
Sodium silicate	8.00	8.00	8.00
Boric acid	7.50	7.50	7.50
Kelzan	0.70	0.70	0.70

Table 9

The values of resistance to the saline mist measured are summarized in table 10 below.

	Composition C	Composition D	Composition E
Weight of layer (g/m <sup>2</sup> )	21	22.5	20.5
Red rust (number of hours)	170	310	430

Table 10

**Example 10:** process of introduction of chelated organic titanates or zirconates, compatible in aqueous phase, into an aqueous phase - co-hydrolysis with the silane:

a) titanates

i) preparation of the aqueous phase:

10 parts by weight of TYZOR® TEP (supplied by DuPont de Nemours, 60% dry extract) and 25 parts by weight of silane A-187 are mixed with magnetic stirring for one hour. 113 parts by weight of water are then added rapidly and the magnetic stirring is maintained for one hour.

This mixture is then introduced into an aqueous composition constituted of 350 parts by weight of water, 8.8 parts by weight of sodium silicate, 8.2 parts by weight of boric acid and 9 parts by weight of molybdenum oxide.

ii) composition of the organic phase:

The organic phase contains:

20	- dipropylene glycol	75 parts by weight
	- Remcopal N4 100 <sup>12</sup>	14 parts by weight
	- Remcopal N9 1001 <sup>13</sup>	15.5 parts by weight
	- Silane A 187	70 parts by weight
	- Zinc paste	235 parts by weight
25	- Aluminium Stapa <sup>14</sup>	30 parts by weight
	- Schwego foam 8325 <sup>15</sup>	5.5 parts by weight
	- Yttrium oxide <sup>16</sup>	30 parts by weight
	- aerosil 380 <sup>17</sup>	0.4 part by weight

<sup>12</sup> wetting agent of ethoxylated nonylphenol type (CECA)

- 29 -

- <sup>13</sup> wetting agent of ethoxylated nonylphenol type (CECA)  
<sup>14</sup> 80% Chromal VIII in dipropylene glycol, marketed by Eckart Werke  
<sup>15</sup> hydrocarbon-type antifoam (Schwegman)  
<sup>16</sup> Y<sub>2</sub>O<sub>3</sub> of purity equal to 99.99%  
5 <sup>17</sup> anti-sedimentation agent of silica type (Degussa)

iii) results of the saline mist tests:

- Bath according to the invention: anticorrosion coating composition according to the invention: the organic and aqueous phases obtained (steps ii) and i), respectively) are mixed.

- Reference bath: reference composition:

The aqueous phase of the reference composition contains:

	Water	463 parts by weight
15	Sodium silicate 20 N 32	8.8 parts by weight
	Boric acid	8.2 parts by weight
	Molybdenum oxide	9 parts by weight
	Silane A 187	31 parts by weight

The organic phase of the reference composition has the same composition as the organic phase of the bath according to the invention (step ii)).

The saline mist tests are carried out after an ageing of the baths, according to the invention and reference, of the order of 48 hours. The results obtained are given in table 11 below:

	Results on screws (5 <sup>d</sup> /4.8 <sup>e</sup> )			Results on steel support	
	Such as	V+CM <sup>a</sup>	2 x G <sup>b</sup>	Sacrificial protection <sup>c</sup>	2xG <sup>b</sup>
Reference bath	672/672	456/840	168/336	624	168
Bath according to the invention	> 1150	840/912	336/576	1150	744

Table 11

<sup>a</sup> V + CM: saline mist results after the screws had been subjected to the mechanical shocks of vibrations and falls.

<sup>b</sup> 2 x G: saline mist results after the screws or the plates had been subjected twice to chipping, that is to say a  
5 spattering of impacts.

<sup>c</sup> Sacrificial protection: number of hours of exposure to the saline mist, without red rust after incision of the coating to the metal.

<sup>d</sup> notation 5: results corresponding to less than 1% of red  
10 rust on surface.

<sup>e</sup> notation 4.8: results corresponding to less than 5% of red rust on surface.

Table 11 makes it appear clear that the introduction of chelated organic titanate, compatible in aqueous phase, co-  
15 hydrolysed with the silane in the coating compositions increases the good behaviour to saline mist of the samples treated by these compositions.